

Research Article

Investigation by Raman Spectroscopy of the Decomposition Process of HKUST-1 upon Exposure to Air

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We report an experimental investigation by Raman spectroscopy of the decomposition process of Metal-Organic Framework (MOF) HKUST-1 upon exposure to air moisture ($T = 300$ K, 70% relative humidity). The data collected here are compared with the indications obtained from a model of the process of decomposition of this material proposed in literature. In agreement with that model, the reported Raman measurements indicate that for exposure times longer than 20 days relevant irreversible processes take place, which are related to the occurrence of the hydrolysis of Cu-O bonds. These processes induce small but detectable variations of the peak positions and intensities of the main Raman bands of the material, which can be related to Cu-Cu, Cu-O, and O-C-O stretching modes. The critical analyses of these changes have permitted us to obtain a more detailed description of the process of decomposition taking place in HKUST-1 upon interaction with moisture. Furthermore, the reported Raman data give further strong support to the recently proposed model of decomposition of HKUST-1, contributing significantly to the development of a complete picture of the properties of this considerable deleterious effect.

1. Introduction

Metal-Organic Frameworks (MOFs) are a new class of hybrid compounds constituted by combination of metallic clusters and organic linkers [1–4]. The formation of a crystalline porous matrix is achieved by reacting these two basic elements in appropriate synthesis conditions [1–4]. The possibility to adapt crystalline structures to a specific request, in terms of appropriate choice of metallic centers, linkers length, pore dimensions, and high surface area, makes MOFs very interesting in a wide range of application fields as catalysis and biomedical field as drug delivery systems, chemical sensors, gas storage, and so on [1–4].

One of the most promising MOFs from the point of view of fundamental and applied research is HKUST-1, synthesized for the first time in 1999 [5]. It is a reference material for adsorption of small molecules and gases and selective capture and transporting of a large variety of gases. In particular, several recent studies have been focused on the

hydrogen, methane, and carbon dioxide storage in order to use alternative clean energy sources and with the intent to eliminate greenhouse gases from the atmosphere [6–9].

The outstanding adsorption properties of HKUST-1 are strictly related to its structural characteristics. Indeed, the cubic crystalline structure of this material, whose chemical composition is $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$, is composed of two Cu^{2+} ions linked together by four carboxylate groups to form a paddle-wheel unit. Each carboxylate bridge is part of 1,3,5-benzene tricarboxylate (BTC) linker molecule. A picture of this structure is reported in Figure 1.

The crystal structure involves large cavities with diameter of about 9 Å and small pockets with diameter of about 6 Å. The principal adsorption sites of polar molecules as NH_3 and H_2O are those located on axial binding site of Cu^{2+} ion, called open metal sites [5].

The good affinity of HKUST-1 with respect to water molecules has been extensively investigated in the past. Indeed, it is well known that the adsorption of water molecules

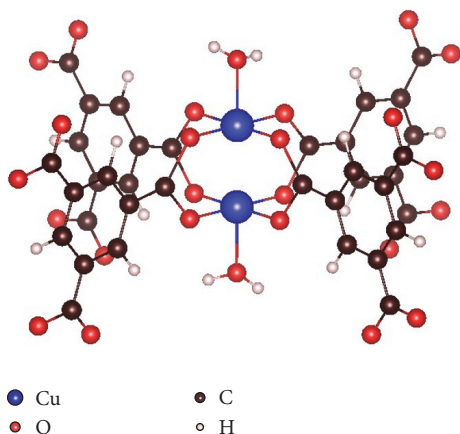


FIGURE 1: Schematic representation of the paddle-wheel unit of as synthesized HKUST-1. Each Cu^{2+} ion is coordinated with four carboxylate groups, belonging to four 1,3,5-benzenetricarboxylate (BTC) linker molecules and one water molecule.

on open metal sites actually takes place within few minutes of exposure to moisture [10]. This feature has been already taken into account in industrial applications because, for instance, the absorption of some gases is assisted by the presence of water molecules in matrix [11, 12].

In spite of this, one of the crucial aspects to consider is the stability of HKUST-1 with respect to a prolonged exposure to moisture, which can affect the crystalline matrix [13, 14]. Indeed, the range of applications of a MOF is significantly reduced if the integrity of the crystalline matrix is compromised as a consequence of such treatments. In fact, some studies have pointed out that HKUST-1 is not much stable with respect to moisture. In particular, it has been shown that when the material is exposed to moisture, it adsorbs a lot of water molecules until they reach the liquid state into the cavities. When this stage is obtained, water becomes able to hydrolyze the Cu-O bonds, breaking the crystalline network of the material. Recently, the effects of the interaction of HKUST-1 with air moisture ($T = 300\text{ K}$, 70% relative humidity) for a long period of time have been investigated in detail by electron paramagnetic resonance (EPR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and surface analysis techniques. It has been shown that the decomposition process of HKUST-1 upon exposure to moisture takes place through three different stages. The first stage, with duration of about 20 days, is characterized by the adsorption of a large amount of water molecules by the material. Water molecules gradually fill the cavities of the material pushing towards the Cu^{2+} ions. The authors [15] pointed out by XRD that during this first stage the material undergoes a swelling, but no irreversible structural changes take place in the material. The decomposition process of the crystalline matrix actually starts for times longer than 20 days, when the effects of the hydrolysis of the Cu-O on the structure of the material become more and more evident on increasing the duration of exposure to air [15]. In particular, during the second stage of the process of decomposition, which takes place for exposure times from 20 days to 50

days, about 35% of the paddle-wheels become hydrolyzed and consequently one of the four carboxylate bridges involved in these paddle-wheels is detached. Finally, in the third stage of the process of decomposition, which takes place for exposure times longer than 50 days, a second detaching of a carboxylate bridge takes place in the same paddle-wheels already affected in the previous stage of the process.

In order to shed new light on the fundamental issue concerning the structural effects induced by hydrolysis on carboxylate MOFs, here we present an experimental investigation performed by Raman spectroscopy focused on the process of decomposition induced in HKUST-1 upon exposure to air moisture ($T = 300\text{ K}$, 70% relative humidity) and showing the potentialities of the technique to deepen the understanding of the underneath process in terms of molecular groups changes.

2. Materials and Methods

Commercial HKUST-1 in powder form was purchased from Sigma-Aldrich as Basolite C300. A sample of about 10 mg of HKUST-1 was exposed to air at $T = 300\text{ K}$ and relative humidity (RH) of 70% for different times. We have monitored the vibrational properties of the sample of HKUST-1 with Raman spectroscopy from about 3 hours up to 165 days of exposure to air. Furthermore, we have performed a measurement on the activated sample of HKUST-1.

The Raman measurements were acquired in the region from 150 to 1700 cm^{-1} with a Bruker Senterra μ -Raman spectrometer equipped with a diode laser working at $\lambda = 532\text{ nm}$. We have performed measurements both at high resolution ($3\text{--}5\text{ cm}^{-1}$) and at low resolution ($9\text{--}15\text{ cm}^{-1}$). The advantage of the low resolution mode is that it gives spectra with significantly higher signal-to-noise ratio with respect to those obtained in high resolution mode. The nominal laser power was 0.2 mW to avoid sample modifications. For statistical reasons, each sample was measured in three different points and the resulting spectra were averaged.

The spectrum of the activated sample of HKUST-1 was acquired with a Horiba LabRam HR-Evolution μ -Raman spectrometer with a 532 nm laser and 1 mW nominal laser power, at high resolution (4 cm^{-1}). No spectral distortions were induced by laser power.

The sample was put inside a high pressure Linkam THMS600PS cell at 150°C (heating ramp 100 C/min) in atmospheric pressure and monitored starting from 10 minutes up to 1 hour, recording Raman spectra.

All the recorded spectra were subtracted by a baseline and subsequently normalized with respect to the intensity of the band at $\sim 1000\text{ cm}^{-1}$. We have chosen this peak for the normalization because it is well known that it is a very stable signal as it is related to the symmetric stretching of the C=C bonds in the rigid benzene rings.

3. Results

The high resolution Raman spectrum of the sample of activated HKUST-1 and that acquired for the sample after

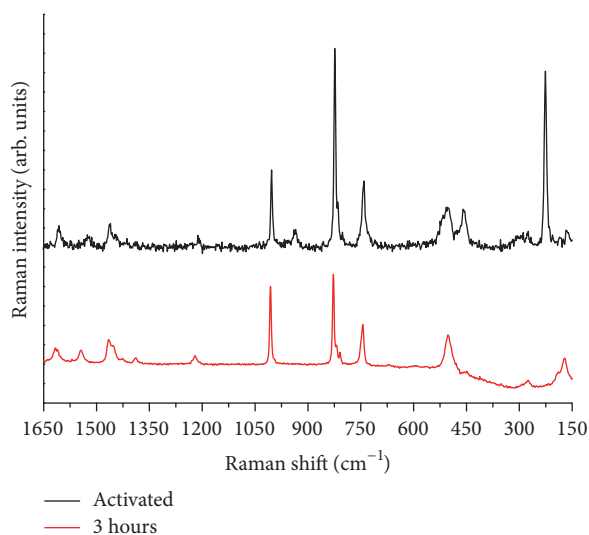


FIGURE 2: High resolution Raman spectra of the HKUST-1 sample activated (black line) and after about 3 hours of exposure to air moisture at $T = 300$ K (red line). Spectra are vertically shifted, for viewing purposes, after the normalization described in the text.

about 3 hours of exposure to air ($T = 300$ K, RH 70%) are reported in Figure 2.

The two spectra show the same spectroscopic characteristics with respect to those reported in literature for activated and hydrated HKUST-1 [16, 17]. In particular, the intense peak at about 230 cm^{-1} evident in the spectrum of activated sample is replaced by two bands in that of the sample exposed to air for 3 hours, in line with results reported by other authors [16].

Regarding the spectrum of the sample exposed to air for 3 hours, between 150 and 600 cm^{-1} , the peaks of vibrational modes involving Cu^{2+} ions are evident. More precisely, the doublet at $173\text{--}191\text{ cm}^{-1}$ and the peak at 276 cm^{-1} are assigned in literature to a stretching mode involving Cu-Cu dimer and Cu-O_w, where O_w indicates the oxygen of the water molecule adsorbed on Cu^{2+} ion, respectively [16–19]. The doublet at $449\text{--}502\text{ cm}^{-1}$, whose first component is barely detectable, is related to Cu-O stretching modes involving oxygen atoms of carboxylate bridges [16, 17].

In the central region from 700 to 1100 cm^{-1} , it is possible to recognize the peaks related to the vibrational modes of benzene rings. In particular, at 745 cm^{-1} and at 828 cm^{-1} , we observe the C-H out-of-plane bending modes of rings, whereas at 1006 cm^{-1} the symmetric stretching mode of C=C is well evident in the Raman spectrum [16–19]. In the region from 1400 to 1700 cm^{-1} , two vibrational modes of carboxylate bridges are present. The first feature at 1460 cm^{-1} corresponds to the symmetric stretching of O-C-O, whereas the peak at 1544 cm^{-1} corresponds to the asymmetric stretching of O-C-O [16]. At 1616 cm^{-1} , the C=C symmetric stretching of benzene ring is recognized [16, 17].

In Figure 3, a comparison of the Raman spectra obtained for the HKUST-1 exposed to air moisture ($T = 300$ K, RH 70%) for different times is reported.

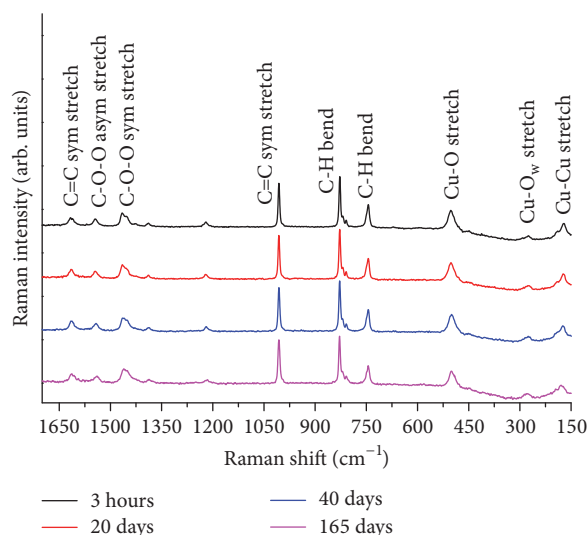


FIGURE 3: High resolution Raman spectra of HKUST-1 acquired after about 3 hours and 20, 40, and 165 days of exposure to air at $T = 300$ K. Spectra are vertically shifted, for viewing purposes, after the normalization described in the text.

As shown in Figure 3, the Raman spectrum obtained for the sample exposed to air for about 3 hours contains essentially the same peaks as the spectra obtained after longer exposure to air up to 165 days. This indicates that no new vibrations are induced by the decomposition process of the material in the investigated wavenumbers range. In order to obtain a more detailed description of the variations induced in the Raman spectra of HKUST-1 during the exposure of the material to air, we have estimated the intensity and the position of all the relevant peaks present in the Raman spectra. For this analysis we have taken advantages of the high signal-to-noise ratio of the spectra obtained in the low resolution mode.

In Figure 4, the variations induced by exposure of HKUST-1 to air in the intensity and in the position of the peak at about 174 cm^{-1} attributed to a mode involving the Cu-Cu stretching, are presented. A comparison among some indicative spectra in the region of this peak is also reported in Figure 4(b). As shown, we observe that both the amplitude and the peak position of this band remain almost constant up to about 20 days of exposure to moisture. At variance, Figure 4(a) suggests that for longer exposures the peak position undergoes a blue shift and correspondingly the peak amplitude decreases. However, by inspection of the spectra of Figure 4(b), it is easy to recognize that actually the situation is more complex. In fact, it emerges that in correspondence between the longest exposure times the peak exhibits at least two well distinguishable components, both peaked at larger wavenumbers with respect to the position observed after 3 hours of exposure of the material to air moisture.

Similarly, in Figure 5, the changes induced in the peak at about 502 cm^{-1} related to Cu-O stretching are reported. As shown, in this case we have found that this feature remains stable up to about 20 days of exposure to air; thereafter both

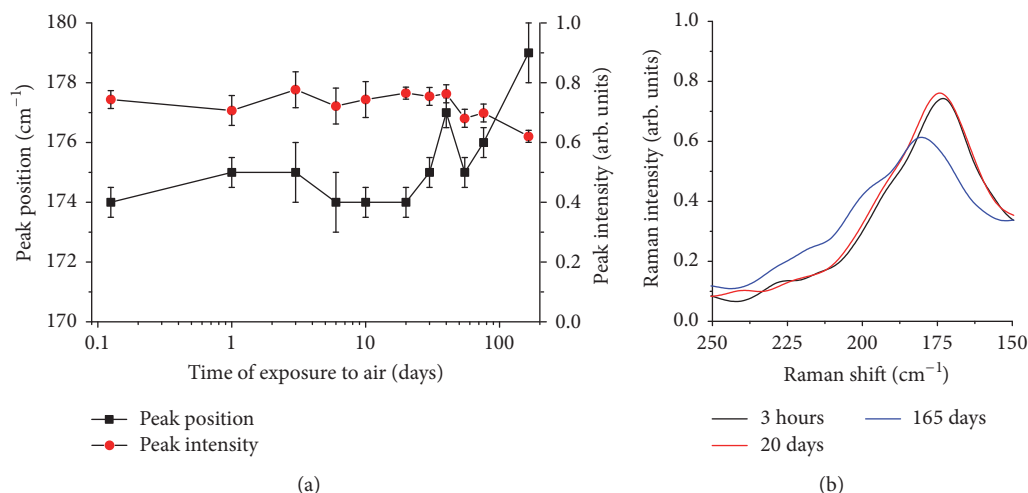


FIGURE 4: (a) Position (black squares) and intensity (red circles) of the Raman peak at about 174 cm⁻¹ for HKUST-1 as a function of time of exposure to air moisture. (b) Raman spectra in the region of the peak at about 174 cm⁻¹ acquired for HKUST-1 after 3 hours, 20 days, and 165 days of exposure to air moisture.

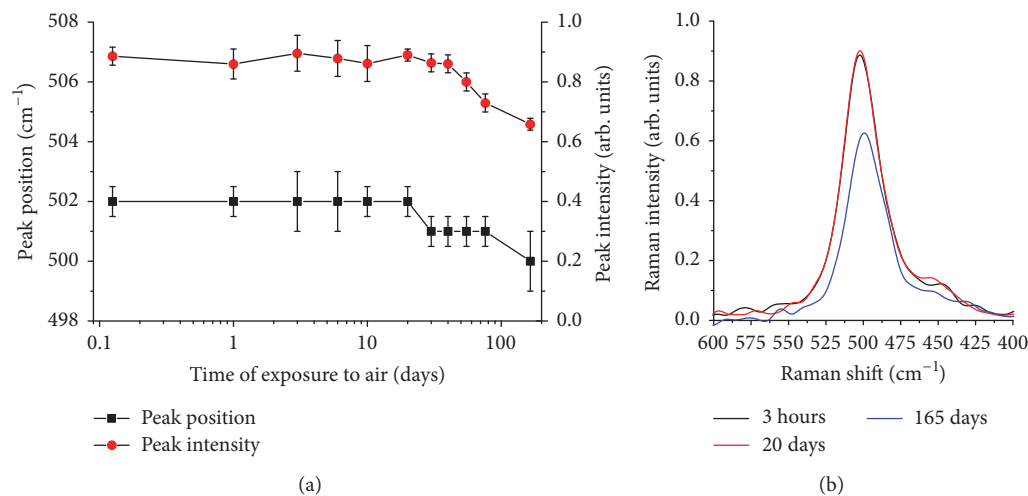


FIGURE 5: (a) Position (black squares) and intensity (red circles) of the Raman peak at about 502 cm⁻¹ for HKUST-1 as a function of time of exposure to air moisture. (b) Raman spectra in the region of the peak at about 502 cm⁻¹ acquired for the HKUST-1 after 3 hours, 20 days, and 165 days of exposure to air moisture.

the amplitude and the position of the peak gradually change. The former reduces from 0.88 to 0.64 for exposure to air up to 165 days, whereas the latter undergoes a red shift of about 2 cm⁻¹. This shift is small but well reliable, as it falls above the experimental uncertainty, as it is evident from Figure 5(a). The amplitude difference of the peak at about 502 cm⁻¹ between spectra at 20 and 165 days of exposure to moisture is well recognizable in Figure 5(b).

Finally, in Figure 6, the data concerning the peak at about 1615 cm⁻¹ are summarized. In this case we observe that the peak position remains essentially unchanged during the first 20 days of exposure of the material to air, whereas it undergoes a red shift for longer exposure times. The maximum shift observed for this band is of about 2 cm⁻¹. At variance, no relevant changes of the peak intensity take place

during 165 days of exposure of the material to air moisture. Features similar to those here described were also found for the peaks at 1460 cm⁻¹ and at 1544 cm⁻¹ due to the symmetric and asymmetric stretching of O-C-O groups. All the other peaks not mentioned above were found to be essentially not affected by the exposure of the material to air moisture up to 165 days and will not be considered further.

4. Discussion

The main purpose of the present investigation is to better understand the processes of decomposition taking place in the carboxylate MOF HKUST-1 upon exposure to air moisture. Since in a recent work [15] a model has been proposed for this process, here we expect to find further support to

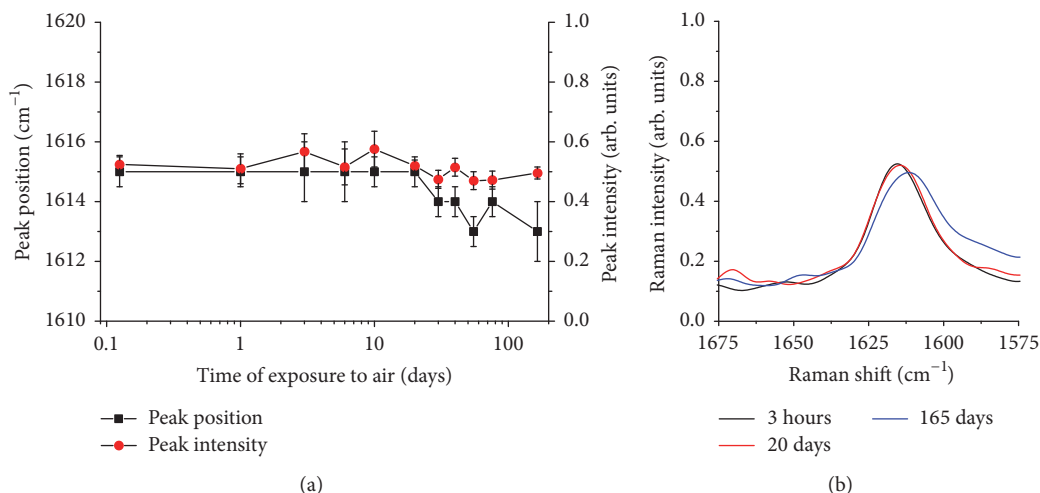


FIGURE 6: (a) Position (black squares) and intensity (red circles) of the Raman peak at about 1615 cm⁻¹ for HKUST-1 as a function of time of exposure to air moisture. (b) Raman spectra in the region of the peak at about 1615 cm⁻¹ acquired for HKUST-1 after 3 hours, 20 days, and 165 days of exposure to air moisture.

that model and to obtain a more detailed knowledge of the process. This goal is actually achieved by the overall data presented in the previous section and discussed in detail in the following.

The proposed model indicates that, during the first 20 days of exposure of HKUST-1 to air moisture, no irreversible processes take place. In fact, during this first stage, large quantities of water molecules are absorbed by the material, just filling the volume of the cavities. In agreement with the expectation that no irreversible changes take place during the first 20 days of exposure, the Raman data reported here indicate no relevant changes affecting the peaks falling within the range of investigated wavenumbers. Model [15] also suggests that, during this first stage of the process, the electronic energy levels of the Cu²⁺ ions significantly change and that the interaction between the two Cu²⁺ ions within the paddle-wheels becomes stronger, as a consequence of the interaction of these ions with the large quantities of water filling the cavities and pushing in all directions. This effect is actually not caught by the Raman spectroscopy in the present investigation, as no change in the properties of the Cu-Cu vibration is recognized. The reason for this failure is probably due to the fact that the two Cu²⁺ are very far away with respect to each other and consequently their bond strength is expected to be very weak. In fact, the estimated distance between them is of about 2.64 Å [16]. Since the variations of the properties of this bond induced by exposure of the material to air moisture are expected to be small perturbations of the pristine small value, they presumably fall below the detection limit of our Raman equipment.

On the basis of previous reports [15, 18, 19], it is known that upon exposure of HKUST-1 to air moisture for times between 20 and 40 days the irreversible process of hydrolysis of the Cu-O bonds is active. As a consequence of this process one of the four carboxylate bridges is detached in about 35% of the paddle-wheels of the material, generating a paramagnetic defect named E₁'(Cu) center, which involves

a Cu ion in +1 oxidation state with reduced coordination and a Cu²⁺ ion with the pristine coordination but modified environment [15]. Finally, the last stage of the process of decomposition of HKUST-1 starts for exposure times longer than 50 days and it involves a further detaching of a second carboxylate bridge in the same paddle-wheels already affected in the previous stage of the process [15]. Such final structure has been attributed to a paramagnetic defect named E₂'(Cu) center. The occurrence of relevant irreversible modification of the material for exposure times longer than 20 days is actually confirmed by the reported Raman data. As shown in Figures 4, 5, and 6, some of the Raman bands suffer detectable peak shifts for such exposure times. More in detail, the blue shift of the peak related to the Cu-Cu bonds shown in Figure 4 indicates that the structure of the dimer significantly changes after prolonged exposure to air moisture. In addition, the fact that this peak exhibits two distinguishable components after 165 days of exposure is very interesting, as it indicates that the paddle-wheels of the material are of two different types, with different structures, and characterized by well distinguishable Cu-Cu vibrations. The presence of two structures presumably corresponds to the hydrolyzed and nonhydrolyzed paddle-wheels, within the pristine structure. On the basis of the model [15], the relative weight of these two components is about 35% and 65%, respectively. These quantities are roughly consistent with the relative amplitude of the two components shown in Figure 4 in the range from 150 cm⁻¹ to 200 cm⁻¹. By careful inspection of the peak at about 174 cm⁻¹ for the spectra obtained for HKUST-1 exposed to air moisture for about 3 hours and 20 days shown in Figure 4(b), a very small shoulder is recognized at about 178 cm⁻¹. This feature is presumably due to a small fraction of preexisting defective paddle-wheels essentially generated during the synthesis of the material. Concerning the properties of the Cu-O bonds, together with a notable red shift, it also suffers a considerable reduction of the peak intensity for exposure times longer than 20 days. This interesting result agrees with the model,

indicating that after hydrolysis many Cu^{+1} ions suffer a reduction of their coordination number with respect to the pristine structure.

Finally, we note that since the hydrolysis process involves the oxygen of the carboxylate bridge, one expects also to observe a change of the spectroscopic properties of the peaks at 1460 cm^{-1} and at 1544 cm^{-1} , corresponding to the symmetric and asymmetric stretching of O-C-O groups. Also this expectation has been fulfilled in our present investigation. As a matter of fact, we have observed a gradual red shift of these bands for long exposure times of the material to air. It is worth noticing that, in agreement with the model of decomposition proposed previously [15], we have observed no change of the intensities of these two bands. This is due to the decomposition process of the material that does not change the number of carboxylate bridges but just the properties of their pristine coordination with the Cu^{2+} ions. We have found similar changes in the peak at 1615 cm^{-1} due to the stretching mode of C=C bonds of the benzene ring. This is not surprising because such vibrations actually take place in the aromatic ring of the linker and consequently the modifications occurring in the carboxylate bridges are expected to affect indirectly also the C=C vibration properties. Also, in this case, no change in the number of the C=C bonds is expected. Accordingly, as shown in Figure 6, there is no change of the intensity of the peak at 1615 cm^{-1} is recognized.

5. Conclusions

We report an experimental investigation by Raman spectroscopy of the decomposition process induced by exposure of the MOF HKUST-1 to air moisture. Our data indicate the occurrence of relevant structural processes taking place in the material for exposure times longer than 20 days. In agreement with previous reports [15] these processes are related to hydrolysis which affects a significant fraction of the Cu-O bonds of the crystal, irreversibly reducing the crystalline order of HKUST-1. The coexistence of two types of paddle-wheels with different structures, corresponding to hydrolyzed and nonhydrolyzed paddle-wheels, predicted by a previous study [15], has been confirmed by detecting a splitting of the Raman peak attributed to the Cu-Cu vibration in two well distinguishable components. The predicted change of the coordination number of a fraction of Cu ions in the material during the decomposition process [15] is also confirmed by the observation of a reduction of the intensity of the Raman peak at 502 cm^{-1} , attributed to Cu-O stretching. Summarizing, the overall data reported here support and extend the model of the process of decomposition of HKUST-1 upon exposure to air recently proposed, contributing to reach a complete and reliable description of this technologically relevant process.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

Acknowledgments

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